

The University of Chicago

I

A STUDY OF FREE RADICALS

II

A METHOD FOR DETERMINING THE STRUCTURE OF ORGANIC STANNONIC ACIDS AND A NEW METHOD OF PREPARATION OF ORGANO-MERCURI COMPOUNDS

A DISSERTATION SUBMITTED TO THE
GRADUATE FACULTY IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1929

By

MORRIS HYMAN DASKAIS

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I
A STUDY OF FREE RADICALS

In 1900 Gomberg¹ discovered a hydrocarbon which seemed to behave as a compound of trivalent carbon, i.e., triphenylmethyl, as the result of an investigation which was undertaken with a view to establish definitely the constitution of tetraphenylmethane. The problem as conceived by Gomberg involved the preparation of hexaphenylethane and since the Fittig synthesis and the other usual methods had failed to give this hydrocarbon, Gomberg tried to prepare it by treating triphenylchloromethane and triphenylbromomethane with finely divided metals such as mercury and molecular silver. This led to the finding of triphenylmethyl peroxide and subsequently to the discovery of the dissociation of hexaphenylethane into two triphenylmethyl radicals. This work opened up one of the most fascinating and fertile fields of modern organic chemistry.

The existence of organic free radicals of so-called trivalent carbon, however, was not accepted on the basis of Gomberg's work alone. It was ten years later when Schlenk² prepared the diphenylbiphenylmethyl, phenyldibiphenylmethyl and the tri-biphenylmethyl radicals that this concept of trivalent carbon received universal recognition. But even with the preparation of over a hundred of these so-called free radicals and detailed studies and researches on their properties, to date there is no satisfactory hypothesis which explains the cause of the dissociation of the hexa-arylethanes or predicts the relationship between structure and extent of dissociation.

Several investigators have advanced hypotheses attempting to correlate the extent of dissociation of hexa-arylethanes into triarylmethyl radicals with varying degrees of success. Of these, in a recent discussion, Gomberg³ says,

¹Gomberg, J.A.C.S., 22, 757 (1900).

²Schlenk, Ber., 55, 2291, 2299 (1922).

³Gomberg, Chem. Rev., I, 104 (1924).

From Schlenk's results with biphenylhexa-arylethanes one might infer that the dissociation of the hexa-arylethane into free radicals is greatly favored by the complexity or the weight of the aryl groups, the dissociation becoming apparently more manifest also in proportion to the number of such groups. Some support in favor of this inference is given by the α -naphthylidiphenylmethyl radical, which was found to be monomolecular to the extent of 60%. But the hypothesis that the dissociation of the hexa-arylethanes is proportional to the complexity of the aryl groups becomes wholly untenable, when one compares triphenylmethyl (5% dissociated) with phenylxanthyl, which is monomolecular to the extent of 75%. . . . More facts are needed before we can hope to unravel this confusing interplay of various influences.

Within the past few years, a new notion concerning the types of bonds between carbon atoms, based on the relative electronegativity of organic radicals, has been advanced by Kharasch and coworkers,⁴ which readily lends itself to the interpretation of these phenomena. According to this concept, the type of bond represented by the two methyl carbon atoms of hexaphenylethane is that of two weakly electronegative radicals and relatively unstable. The degree of instability is so great that the increment of energy necessary to rupture the bond is so small that hexaphenylethane will dissociate to some extent at room temperature.

From this same viewpoint, it is obvious that the stability of the bond between the two methyl carbon atoms in any substituted ethane could be determined from a consideration of the degree of electronegativity of the organic radicals. Kharasch and Marker⁵ have shown the effect of attachments of various groups to a single carbon atom. The substitution of a comparatively electronegative substituent such as the phenyl radical for an hydrogen atom of a methyl radical results in a marked decrease in the electronegativity of the group as a whole. Thus, the benzyl radical is less electronegative than the methyl. Furthermore, the substitution of another phenyl for an hydrogen atom of the benzyl radical, forming the diphenylmethyl radical still further decreases the electronegativity of the methyl carbon atom. Graphically this may be represented as in Figure 1:

⁴Kharasch and Sher, J. Phys. Chem., **29**, 625 (1925); Kharasch and Marker, J.A.C.S., **48**, 3130 (1926).

⁵Kharasch and Marker, J.A.C.S., **48**, 3130 (1928).

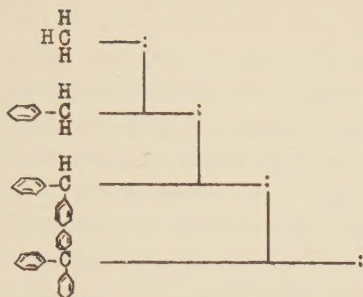


Figure 1.

If the hydrogen atoms of the methyl group are replaced by radicals more electronegative than phenyl, the radical X_3C (where X represents a group more electronegative than phenyl) should be less electronegative than triphenylmethyl. The more strongly electronegative X is, the less electronegative does the methyl group X_3C become.

Upon this basis the facts cited in Gomberg's article on "Organic Radicals"⁶ are readily explainable. In connection with those remarks I take the liberty of quoting at some length from the above mentioned paper of Kharasch and Marker.⁷

Reference to the tables in the article mentioned will disclose the fact that radicals which in the Table of Electronegativity lie above the phenyl radical increase dissociation, while those below the phenyl radical hinder or stop it completely. It is also instructive to note that since the diphenyl radical is more electronegative than the phenyl radical, it increases the dissociation of the hexa-aryl ethane much more than the phenyl radical. The fact also that the α -naphthyl radical is more electronegative than the β -naphthyl radical causes it to be more potent in causing dissociation of the hexa-aryl ethane molecule.

According to our hypothesis the weight or complexity of the radical is of no significance in this case and no logical deductions can be made from it; it is the electronegativity of the radical attached to the methyl carbon atom (with the consequent decrease in the electronegativity of the methyl group) that is of paramount importance. That is the reason the cyclohexyl radical decreases dissociation of the aryl ethane while the naphthyl radical increases it, although both of them are heavier than the phenyl radical, and the

⁶Gomberg, Chem. Rev., I, 105 (1924).

⁷Kharasch and Marker, loc. cit.

reason the α -naphthyl increases dissociation more than the β -naphthyl radical, for the former is the more negative radical.

Since it was possible to predict which hexa-arylethanes would dissociate to a greater extent than hexaphenylethane, by substituting more electronegative groups than phenyl for phenyl, it follows that the concept likewise predicts hexa-arylethanes which should dissociate to a lesser extent than hexaphenylethane. These compounds should be realized by the substitution of less electronegative groups than phenyl for phenyl in hexaphenylethane. Very few such radicals have as yet been placed in the table of electronegativity. It is known that hexamethylethane does not dissociate. Hence the radicals between phenyl and methyl constitute the groups which when substituted for the phenyl radicals in hexaphenylethane, should dissociate less than hexaphenylethane, if they show any dissociation at all.

Kharasch and Flenner⁸ have determined the relative electronegativity of the ortho, meta and para chlorophenyl radicals and arranged them as in Figure 2, when compared with the phenyl and methyl radicals:

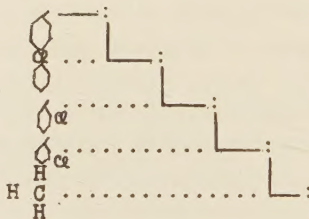


Figure 2.

Thus, since the metachlorophenyl radical is the least electronegative of the aryl groups mentioned, if the concept is correct, hexametachlorohexaphenylethane should dissociate to a lesser extent than hexaphenylethane. Hence the purpose of this investigation was to prepare hexametachlorohexaphenylethane and study the extent of its dissociation. The usual method of preparation of hexa-arylethane is through the intermediate steps of

⁸Kharasch and Flenner, Private communication.

the triarylcarbinol which is converted into the chloride by means of dry hydrogen chloride or acetyl chloride in benzene solution. The triaryl chloride is purified, dissolved in dry benzene and then shaken with molecular silver or mercury in the absence of air, yielding the hexa-arylethane.

The general method described above was followed. Thus, dimetachlorobenzophenone was made by the condensation of one mole of metachlorophenyl magnesium bromide with an equivalent weight of metachlorobenzoyl chloride, the Grignard reagent being added to the ethereal solution of the acid chloride. The first few attempts to prepare this ketone resulted in viscous oils, whose crystallization was accomplished only after inoculation with crystals of benzophenone. After the first crystalline batch was prepared, the substance thereafter was always obtained in crystalline form directly on evaporation of the solvent.

Dimetachlorobenzophenone was condensed with one mole of metachlorophenyl magnesium bromide. The reaction product when hydrolyzed gave presumably trimetachlorotriphenylcarbinol. In all attempts to prepare the above carbinol an uncrystallizable oil was obtained. Efforts to crystallize this carbinol, such as distillation in high vacuo, slow evaporation of solvents from its solutions, inoculation with triphenylcarbinol, supercooling and many other of the usual methods of forcing crystallization were of no avail.

I next attempted to make trimetachlorotriphenylmethyl chloride from the impure carbinol. The same difficulties were encountered in trying to crystallize the chloride. I tried to prepare the stannic chloride and ferric chloride double salts in the endeavor to obtain crystalline products, with negative results.

Since the pure carbinol or chloride could not be isolated, the usual methods for the preparation of the free radical could not be used. Hence a modification of Conant's⁹ method was employed. The impure chloride was dissolved in acetone and treated with a solution of freshly prepared vanadous chloride in acetone and glacial acetic acid. The reaction mixture was extracted with chloroform. This extract was evaporated by conducting a stream of oxygen over it. There remained a gummy residue which, however, became crystalline after repeated washings with petroleum ether.

⁹Conant, J.A.C.S., 47, 1970 (1925).

Analyses have shown this compound was the expected trimeta-chlorotriphenylmethyl peroxide. The fact that both carbinol and chloride are soluble in petroleum ether may have aided in the purification of the peroxide.

The formation of a peroxide as described above is indicative of the fact that hexametachlorohexaphenylethane does dissociate. The extent of its dissociation, however, has not been determined. It may only dissociate to a fraction of one per cent, but since the ethane is assumed to be in tautomeric equilibrium with that small fraction of free radical, peroxide formation would continue until all of the ethane was utilized. The slow formation of the peroxide may indicate that only a small fraction exists as the free radical but this assumption must be substantiated by more conclusive experimental evidence.

Work along this line is to be carried on in the near future in the endeavor to measure quantitatively the dissociation of this interesting hexa-arylethane.

EXPERIMENTAL PART

The preparation of metachlorobromobenzene.--A mixture of 35 g. of crystallized cupric sulfate, 12 g. of electrolytic copper, 90 g. of sodium bromide, 20 g. of concentrated sulfuric acid (specific gravity 1.84) and 550 cc. of water, is refluxed for three or four hours until the color becomes yellowish.

When the hydrobromic acid-cuprous bromide solution is ready for use, the diazonium sulfate solution is prepared. A fine suspension of metachloroaniline sulfate is obtained by slowly adding 64 g. of metachloroaniline to a solution of 98 g. of concentrated sulfuric acid in 500 cc. of water, while the solution is strongly agitated. The mixture is cooled below 10°, and diazotized with a solution of 35 g. of sodium nitrite in 63 cc. of water. This operation requires about forty to fifty minutes.

A 5 liter round bottom flask containing the hydrobromic acid-cuprous bromide solution is arranged for steam distillation. After the copper solution is heated to boiling, the diazonium solution is gradually added from a separatory funnel and a vigorous current of steam is passed through the reaction mixture at the same time. The rate of addition of the diazonium salt is so regulated that the time required for the addition is about two

hours. This rate of addition allows a ready interaction and no tarry materials are formed.

The steam distillate and the oil that separates are extracted with ether. The ether layer is separated from the aqueous solution and washed successively with dilute sulfuric acid, sodium carbonate and water. It is then dried over anhydrous sodium sulfate and the whole is filtered. The ether is removed by distillation over a steam bath. The residual oil is distilled under reduced pressure. Yield 58 g.; 60 per cent of calc. yield. The boiling point of this material is 196° at 760 mm. and 82° at 18 mm.

The preparation of metachlorophenyl magnesium bromide.-- This Grignard reagent is prepared by slow addition of an ethereal solution of 1 mole of metachlorobromobenzene to 1.1 moles of magnesium turnings covered with ether. The reaction is started by adding a crystal of iodine and heating with a match flame for one minute. When all the metachlorobromobenzene has been added the whole is refluxed over a water bath for two hours.

The proof of the structure of this Grignard reagent is carried out as follows: Its solution in ether is treated with a solution of mercuric chloride in the same solvent. The mixture is decomposed by pouring it on ice. The whole is then extracted with ether. The product of the reaction is metachlorophenyl mercuric chloride which melts at 165° . This melting point is the same as that of a sample of metachlorophenyl mercuric chloride prepared by Kharasch and Legault¹⁰ by the sulfinic acid method.

Preparation of dimetachlorobenzophenone.--One mole of metachlorophenyl magnesium bromide is added slowly to a solution of 1.2 moles of metachlorobenzoyl chloride in ether. The mixture is frequently shaken during the operation. It is refluxed over a water bath for two or three hours. It is then allowed to cool, treated with a 1 per cent solution of sulfuric acid and extracted with ether. The ether extract is washed several times with sodium carbonate and water. It is then dried over anhydrous sodium sulfate from which it is freed by filtration. The greater part of the ether is distilled from the solution and the last traces removed by evaporation over a steam bath. The solid that separates is crystallized from alcohol twice. Colorless crystals are

¹⁰Kharasch and Legault, Private communication.

obtained only when the alcoholic solution is purified by boiling with Norite. The ketone may also be crystallized from benzene. The melting point is 123° . For analysis the substance was dried in vacuo over phosphoric anhydride. Analyses: Subs. 0.2197, 0.2270; cc. of 0.1 N AgNO_3 17.60, 18.16. Calc. for $\text{C}_{13}\text{H}_8\text{OCl}_2$; Cl 28.29 Found Cl 28.50, 28.54.

Preparation of trimetachlorotriphenyl carbinol.--It was attempted to prepare this carbinol by condensing one mole of metachlorophenyl magnesium bromide with an equivalent quantity of the ketone in ether solution. An oil was obtained in every run. Analyses show the presence of some impurity which evidently prevented the crystallization of this substance. Analyses: Subs. 0.6420, 0.6106; cc. of 0.1 N AgNO_3 49.25, 43.32. Calc. for $\text{C}_{19}\text{H}_{13}\text{OCl}_3$; Cl 29.28 Found Cl 27.43, 25.40.

Preparation of trimetachlorotriphenylmethyl chloride.--The carbinol described above is dissolved in anhydrous ether and converted into the chloride by the action of anhydrous acetyl chloride. Evaporation of the solvent results in an oil which cannot be crystallized. Analyses: Subs. 0.6443, 0.6455; cc. of 0.1 N AgNO_3 57.20, 57.40. Calc. for $\text{C}_{19}\text{H}_{12}\text{OCl}_4$; Cl 37.15 Found Cl 31.64, 31.70.

Preparation of trimetachlorotriphenylmethyl peroxide.--One gram of the above chloride is dissolved in a mixture of 20 cc. of acetone and 10 cc. of glacial acetic acid. The flask containing the solution is swept out with carbondioxide. Ten cubic centimeters of a normal vanadous chloride solution and 8 cc. of concentrated hydrochloric acid are added, the flask being shaken during the addition. To this mixture, 50 cc. of freshly boiled water is added. This precipitates an oil which is presumably hexameta-chlorohexaphenylethane. The whole is extracted with chloroform and the chloroform layer is drawn off into an evaporating dish. The solvent is evaporated by conducting a stream of dry oxygen over the solution. The oil which remains is washed by decantation several times with petroleum ether until a fine crystalline substance is obtained. The peroxide melts at 174° . Analyses: Subs. 0.2396, 0.1948, 0.2480, 0.3312, - - -, 0.004825; cc. of 0.1 N AgNO_3 20.79, 16.62, 20.61, 27.39; CO_2 - - -, 0.01114; H_2O 0.00158. Calc. for $\text{C}_{38}\text{H}_{24}\text{O}_2\text{Cl}_6$; C, 62.87; H, 3.35; Cl, 29.35 Found Cl, 29.31, 30.47, 29.32, 29.15; C, 63.10, 62.97; H, 3.90, 3.66.

The above determinations for carbon and hydrogen were made by Dr. Oskar Wintersteiner, using microchemical methods.

II

A METHOD FOR DETERMINING THE STRUCTURE OF ORGANIC STANNONIC ACIDS AND A NEW METHOD OF PREPARATION OF ORGANO-MERCURI COMPOUNDS

A search of the literature shows that although a few stannonic acids have been known for some time, only one investigation has been made to determine the structure of this general type of compounds. Lambourne¹ contends that methyl stannonic acid is not represented by the simple formula $\text{CH}_3 \cdot \text{SnO} \cdot \text{OH}$, but is probably a complex molecule containing three atoms of tin. He cites the formation of a penta-acetyl and a tri-acetyl derivative of methyl stannonic acid, the analyses of which bear out his claims for a ring structure. This is formed supposedly by the condensation of three molecules of ortho methyl stannonic acid, $\text{CH}_3 \cdot \text{Sn} \cdot (\text{OH})_3$ and the subsequent splitting off of three molecules of water. Hantzsch² believes that tin is quadrivalent in sodium stannite, for which he writes the formula, $\text{H} \cdot \text{SnO} \cdot \text{ONa}$. Lambourne assumes that in the reaction with methyl iodide, a methyl group is substituted for the hydrogen atom. He suggests that the name "sodium stannonate" would be preferable to the commonly used "sodium stannite" in order to distinguish it from the apparently non-existent stannite proper, $\text{Sn}(\text{ONa})_2$.

The purpose of this investigation was to ascertain unquestionably whether in organo-stannonic acids there exists a carbon to tin linkage.

It was proved by Kharasch³ that if tetra-alkyl or tetra-aryl tin compounds are boiled with mercuric acetate all four of the organic groups are taken off the tin and attached to mercury. Therefore it follows that if there is present a carbon to tin linkage in the stannonic acids, similar treatment with mercuric acetate will yield organo-mercuri salts. Such is found to be the case and it is by this means it is proved that there exists a

¹Lambourne, J.C.S., 121, 2533 (1922).

²Hantzsch, Z. phys. Chem., 56, 385 (1906).

³Kharasch, Private communication.

carbon-tin linkage in stannonic acids. To make the evidence conclusive, the stannonic acids used were such as to yield known organo-mercuri salts. This reaction suggests itself as a possible indirect method of preparing mercuri-organic derivatives that cannot be synthesized by known methods.

Methods of preparation of stannonic acids.--Meyer⁴ describes the preparation of ethyl stannonic acid by the reaction of an aqueous solution of sodium stannite with an alcoholic solution of ethyl iodide. He boils the mixture to hasten the reaction and precipitates ethyl stannonic acid by passing a rapid stream of carbon dioxide through the hot alkaline mixture.

Pfeiffer and Lenhardt,⁵ Pope and Peachey,⁶ and Vautin and Stephens,⁷ used the same methods with minor modifications, in their preparation of methyl and ethyl stannonic acids.

Druce⁸ modifies this procedure by using a hot alcoholic solution of stannous chloride to which he adds an excess of an aqueous solution of sodium hydroxide. An alcoholic solution of ethyl bromide is added to the mixture and the whole allowed to stand for three days. Druce suggests that the mixture be shaken at intervals. The alcohol is removed by evaporation over a steam bath, following which ethyl stannonic acid is precipitated by the addition of dilute hydrochloric acid until the mixture is acid to litmus.

In this work, Druce's method was the first to be used in the preparation of ethyl stannonic acid. It seemed to give good yields and to be generally satisfactory. When this product was treated with mercuric acetate, however, repeated experiments yielded only slight traces of ethyl mercuric acetate. However, when ethyl iodide was used in the place of ethyl bromide, large amounts of ethyl mercuric acetate were obtained from the ethyl stannonic acid. Hence it is concluded from these results that Druce's use of alkyl bromides is not to be recommended. However, the addition of a few grams of potassium iodide to a bromide in the preparation of a stannonic acid is found to give satisfactory

⁴Meyer, Ber., 16, 1442 (1889).

⁵Pfeiffer and Lenhardt, Ber., 36, 1054 (1903).

⁶Pope and Peachey, Proc. Roy. Soc., 72, 7 (1903).

⁷Vautin and Stephens, Brit., 294, 287 (Ph) (1927).

⁸Druce, J.C.S., 119, 758 (1921).

results. The method is further modified as follows:

An alcoholic solution of an alkyl iodide or bromide plus potassium iodide is added to an aqueous solution of sodium stannite. The whole is poured into a flask, stoppered tightly and placed in a shaking machine for three days. The alcohol is then removed by gentle evaporation over a water bath and the stannonic acid is precipitated from the resulting mixture by the addition of dilute hydrochloric acid. The material thus obtained is treated with water and the whole centrifuged. Considerable time is saved by this method for washing the precipitate.

The stannonic acids thus prepared are treated with mercuric acetate to give the corresponding alkyl mercuric acetate, which when treated with sodium chloride and potassium iodide is converted into the corresponding alkyl mercuric halides. These salts are purified by crystallization and identified by comparison with known derivatives prepared by other methods.

The problem that next suggested itself was the possibility of placing two stannonic acid groups on the same carbon atom. If this could be done, it might prove to be a means of preparing the corresponding mercury derivatives. Therefore, methylene iodide, iodoform and chloroform were converted into stannonic acids which yielded mercuric halide derivatives. Difficulties were encountered in the identification of these compounds. The evidence, as given in the experimental part, is such that it is believed that the salts, dimercuri-chloro methane $\text{H}_2\text{C}(\text{HgCl})_2$ and dimercuri-iodo methane $\text{H}_2\text{C}(\text{HgI})_2$ have been obtained from methylene stannonic acid. The iodoform derivatives seem to yield methyl mercuric halides. Hence it is assumed that they have been reduced in the usual manner by sodium stannite in the preparation of the stannonic acids.

EXPERIMENTAL PART

The preparation of methyl stannonic acid.--Twenty grams of stannous chloride in 50 cc. of water are added to 100 cc. of a 20 per cent sodium hydroxide solution and the mixture is treated with 14 g. of methyl iodide in 100 cc. of ethyl alcohol. The whole is shaken in a stoppered flask for three days. The alcohol is removed by gentle evaporation over a steam bath. Dilute hydrochloric acid is added until the mixture is acid to litmus. Methyl

stannonic acid separates as a white gelatinous precipitate, which is washed with water until free of stannous ion by repeated centrifuging. It is dried in vacuo over sulfuric acid. Yield 13.5 g.

The preparation of ethyl stannonic acid.--(a) Twenty grams of stannous chloride in 50 cc. of water are added to a 100 cc. of a 20 per cent sodium hydroxide solution and the mixture is treated with 16 g. of ethyl iodide in 100 cc. of ethyl alcohol. The whole is shaken in a stoppered flask for three days. The alcohol is removed by gentle evaporation over a steam bath. Dilute hydrochloric acid is added until the mixture is acid to litmus. Ethyl stannonic acid separates as a white gelatinous precipitate, which is washed with water until free of stannous ion by repeated centrifuging. The acid is dried in vacuo over sulfuric acid. Yield 17 g.

(b) Ethyl stannonic acid is also prepared by using the same method described in (a) except that a mixture of 11 g. of ethyl bromide and 30 g. of potassium iodide is used in place of 16 g. of ethyl iodide. Yield 15 g.

The preparation of benzyl stannonic acid.--Twenty grams of stannous chloride in 50 cc. of water are added to 100 cc. of a 20 per cent sodium hydroxide solution and the mixture is treated with 14 g. of benzyl chloride in 100 cc. of alcohol and 2 g. of potassium iodide. The whole is shaken in a stoppered flask for three days. The alcohol is removed by gentle evaporation over a steam bath. Dilute hydrochloric acid is added until the mixture is acid to litmus. Benzyl stannonic acid separates as a white gelatinous precipitate, which is washed with water until free of stannous ion by repeated centrifuging. Yield 14 g.

Preparation of methylene stannonic acid.--Forty grams of stannous chloride in 100 cc. of water are added to 200 cc. of a 20 per cent sodium hydroxide solution and the mixture is treated with 27 g. of methylene iodide in 200 cc. of alcohol. The whole is shaken in a stoppered flask for three days. The alcohol is removed by gentle evaporation over a steam bath. Dilute hydrochloric acid is added until the mixture is acid to litmus. Methylene stannonic acid separates as a white gelatinous precipitate, which is washed with water until free of stannous ion by repeated centrifuging. Yield 18 g.

Preparation of methylene stannonic acid.--Forty grams of

stannous chloride in 100 cc. of water are added to 200 cc. of a 20 per cent sodium hydroxide solution and the mixture is treated with 26 g. of iodoform or a mixture of 8 g. of chloroform and 2 g. of potassium iodide in 200 cc. of alcohol. The whole is shaken in a stoppered flask for three days. The alcohol is removed by gentle evaporation over a steam bath. Dilute hydrochloric acid is added until the mixture is acid to litmus. Methyline stannonic acid separates as a white gelatinous precipitate, which is washed with water until free of stannous ion by repeated centrifuging. Yield 22 g.

The preparation of methyl mercuric chloride.--A solution of 20 g. of mercuric acetate in 50 cc. of glacial acetic acid is added to 10 g. of methyl stannonic acid. The mixture is refluxed for three or four hours and then transferred to a 1 liter round bottom flask, which is fitted for steam distillation. Steam is vigorously passed through the mixture for about thirty minutes. The residual mixture in the steam distillation flask is filtered. The precipitate, which is largely composed of gelatinous meta stannic acid, is rejected. The addition of a saturated solution of sodium chloride to the filtrate precipitates methyl mercuric chloride, which separates as a fine, white powder. It is removed by filtration. The filtrate is reserved for the preparation of methyl mercuric iodide. The chloride crystallized from alcohol, melts at 170° . Yield 4.5 g.

The preparation of methyl mercuric iodide.--A 10 per cent solution of potassium iodide is added to the filtrate obtained above when methyl mercuric chloride was removed. Methyl mercuric iodide separates as a yellowish white precipitate, which is removed by filtration. It is washed with water containing potassium iodide to remove any occluded mercuric iodide. It is then crystallized from ethyl alcohol. Its melting point is 145° . Yield 5.0 g.

Addition of a solution of potassium iodide to the distillate obtained above will precipitate methyl mercuric iodide as a white crystalline powder, which melts at 145° . Yield 1.0 g.

The preparation of ethyl mercuric chloride.--A solution of 15 g. of mercuric acetate in 50 cc. of glacial acetic acid is added to 12 g. of ethyl stannonic acid. The mixture is refluxed for three or four hours and then transferred to a 1 liter round bottom flask, which is fitted for steam distillation. Steam is

vigorously passed through the mixture for about thirty minutes. The residual mixture in the steam distillation flask is filtered. The precipitate is discarded. The addition of a saturated solution of sodium chloride to the filtrate precipitates methyl mercuric chloride, which separates as a fine white powder. It is removed by filtration. The filtrate is reserved for the preparation of ethyl mercuric iodide. The chloride melts at 191° . Yield 4.0 g.

The preparation of ethyl mercuric iodide.--A 10 per cent solution of potassium iodide is added to the filtrate obtained above when ethyl mercuric chloride was removed. Ethyl mercuric iodide separates as a yellowish white precipitate which is removed by filtration. It is washed with water containing potassium iodide to remove any occluded mercuric iodide. When crystallized from ethyl alcohol, it melts at 179° . Yield 2.0 g.

The preparation of benzyl mercuric iodide.--A solution of 10 g. of mercuric acetate in 35 cc. of glacial acetic acid is added to 9 g. of benzyl stannonic acid. The mixture is gently refluxed for one or two hours over a steam bath and then transferred to a 1 liter round bottom flask, which is fitted for steam distillation. Steam is passed through the mixture for about thirty minutes. The residual mixture in the steam distillation flask is filtered. The precipitate is rejected. The addition of a 10 per cent solution of potassium iodide to the filtrate precipitates benzyl mercuric iodide as a fine, white powder. When crystallized from alcohol, the iodide melts at 115° .

The preparation of dimercuri-chloro methane $H_2C(HgCl)_2$.--A solution of 30 g. of mercuric acetate in 55 cc. of glacial acetic acid is added to 17 g. of methylene stannonic acid. The mixture is gently refluxed for one or two hours and then transferred to a 1 liter round bottom flask which is fitted for steam distillation. Steam is vigorously passed through the mixture for about thirty minutes. The residual mixture in the steam distillation flask is filtered. The precipitate is discarded. The addition of a saturated solution of sodium chloride to this filtrate precipitates a fine, white powder. This powder is placed in a thimble and extracted with hot acetone. The acetone extract is divided into two portions, A and B. The acetone is removed from portion A by spontaneous evaporation. The resulting white crystalline substance is washed with water and alcohol and then

dried in vacuo over phosphoric anhydride. The substance melts at 174° with decomposition. Analyses: Subs. 0.1254, 0.1112; 1 cc. KCNS .009242 g. Hg, cc. KCNS 10.9, 9.7. Calc. for $\text{CH}_2\text{Hg}_2\text{Cl}_2$; Hg. 82.52 Found 80.34, 80.62.

The preparation of dimercuri iodo methane $\text{H}_2\text{C}(\text{HgI})_2$ --A solution of 10 per cent potassium iodide is added to portion B described above. A white precipitate results. The whole is cooled in an ice salt bath and the precipitate is then removed by filtration. This iodide melts at 143° . For analysis it was dried in vacuo over phosphoric anhydride. Analyses: Subs. 0.1635, 0.0719; cc. of KCNS 10.2, 4.6. Calc. for $\text{CH}_2\text{Hg}_2\text{I}_2$; Hg. 59.87 Found Hg. 57.66, 59.13.

Remarks

Mercury halide derivatives were obtained from the stannonic acids prepared from iodoform and chloroform by following the same procedure as outlined above. The mercuric iodide compounds, however, were identified as methyl mercuric iodide by determining melting points of mixtures of them with ethyl mercuric iodide. It is believed that iodoform and chloroform were reduced to methyl iodide and methyl chloride respectively, just as bromoform is reduced to methylene bromide when treated with sodium arsenite.⁹

Conclusions

1. It is proved that a carbon to tin linkage exists in the stannonic acids.
2. The method of preparation of stannonic acids is modified.
3. An indirect method of preparation of organo-mercuri derivatives is devised.

In conclusion I take pleasure in acknowledging gratefully my appreciation of Dr. Kharasch's guidance, encouragement and personal kindness in the course of this work.

⁹See Organic Syntheses, I, 57.

